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16. ABSTRACT

Anomalous NO_x responses were observed when halocarbons were irradiated in the presence of oxides of nitrogen. Interferences to chemiluminescent NO_x monitor using heated carbon converter were studied for phosgene, tri-chloroacetyl chloride, chloroform, chlorine, and hydrochloric acid. Data show positive interferences in the NO_x monitor due to the test compound, either individually or as mixtures. Substituting an $FeSO_4$ converter for the heated carbon converter may solve the problem.

This information may be of particular interest to smog chamber researchers and to those making NO_2 measurements in areas where halocarbon levels are relatively high. It is speculated that excited O_2 molecules may be the interfering compound, but additional work is needed to substantiate this hypothesis.

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JOURNAL ARTICLE

Halocarbon Interferences in Chemiluminescent Measurements of NO_x

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■ Anomalous NO_x responses were observed when halocarbons were irradiated in the presence of oxides of nitrogen. Interferences to a chemiluminescent NO_x monitor using a heated carbon converter were studied for phosgene, trichloroacetyl chloride, chloroform, chlorine, and hydrochloric acid. Data show positive interference in the NO_x monitor due to the test compounds, either individually or as mixtures. Substituting a $FeSO_4$ converter for the heated carbon converter may solve the problem. This information may be of particular interest to smog chamber researchers and to those making NO_2 measurements in areas where halocarbon levels are relatively high. It is speculated that excited O_2 molecules may be the interfering compound, but additional work is needed to substantiate this hypothesis.

Researchers (*1, 2*) have reported that certain commercial chemiluminescent monitors respond to other oxides of nitrogen in addition to NO and NO_2. In this work, we discuss some unusual responses observed by a chemiluminescent NO_x monitor when halocarbons were passed through a heated carbon converter.

Figure 1 shows the data obtained when tetrachloroethylene was irradiated in the presence of NO_x. In Figure 2, similar data are shown for a chloroform/NO_x system. Both experiments were performed in a 440-L borosilicate glass and Teflon smog chamber equipped with fluorescent light banks of blacklights and sunlights. The first order dissociation specific rate for NO_2 for this chamber is 0.5 min^{-1}. Figures 1 and 2 show anomalous NO_2 responses after the halocarbon begins to react. Wet colorimetric analyses for NO_2 (*3*) indicated that both of the experiments showed negligible concentration of NO_2 in the systems. An earlier publication (*4*) on the photooxidation of chlorinated ethylenes reported that HCl, phosgene, and trichloroacetyl chloride are some of the halogen-containing products from the tetrachloroethylene/NO_x system. These compounds were examined for possible interferences to the NO_x mode of the chemiluminescent detectors, i.e., a test gas containing HCl, phosgene, or trichloroacetyl chloride was passed through the heated carbon converter of the NO_x analyzer.

In these experiments Tedlar bags were filled with tank air and spiked with NO/NO_2. In some instances the bags were not spiked with NO/NO_2. The NO_x instrument was then attached to the bag, and the initial NO or NO_2 measurements were obtained. The bags were then spiked with the test halogen-containing compounds, either individually or in mixtures. The

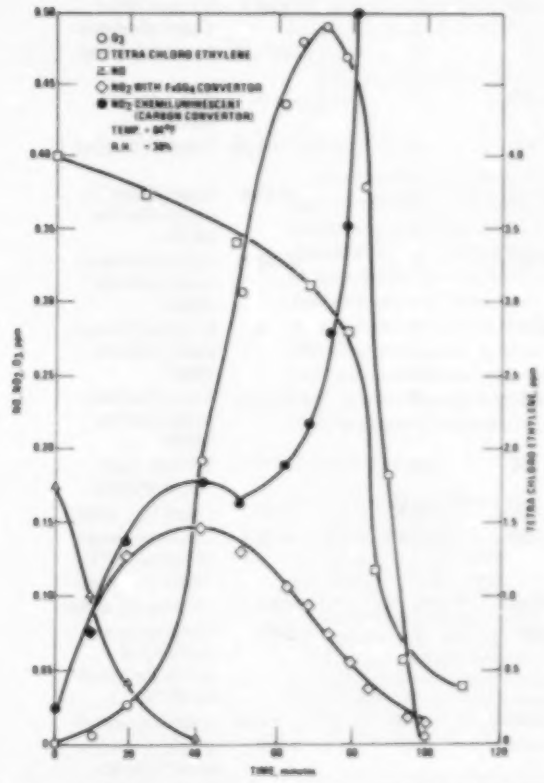

Figure 1. Irradiation of 4 ppm (v/v) tetrachloroethylene and 0.2 ppm NO_x

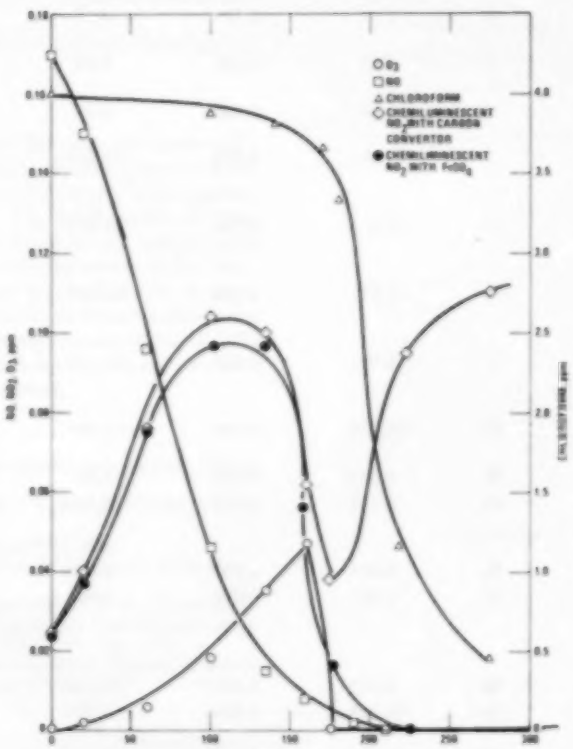

Figure 2. Chloroform (4 ppm) and 0.2 ppm NO_x irradiation

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NO or NO_2 was again measured. The results of the interference studies are shown in Table I. The NO_2 response changes by as much as 330% when phosgene and HCl are added to the NO/NO_2 mixture. Trichloroacetyl chloride also has a similar interference effect. With 5 ppm (v/v) of trichloroacetyl chloride, an interference of approximately 250% was observed when NO_2 was at 0.125 ppm concentration. Chlorine gas also shows an interference for NO_2 measurements. Positive responses were caused by Cl_2 and trichloroacetyl chloride also in the absence of NO_x. Finally, this Cl_2 and halocarbon interference appears to increase with increasing carbon converter temperature.

Chemiluminescent monitors using high-temperature stainless steel converters (such as for monitoring NH_3) may be subject to greater interference for the chlorinated hydrocarbons.

Figure 3 shows the NO_2 response of the chemiluminescent analyzer while monitoring NO_x in an air mixture with increasing concentrations of trichloroacetyl chloride. The interference is practically linear up to 1.1 ppm (v/v) of trichloroacetyl chloride.

The interference problem appears to be eliminated when an $FeSO_4$ converter is used in place of the carbon converter. These data are also shown in Figure 1. However, reported data on an $FeSO_4$ converter operated at room temperature show decreasing efficiency of conversion ($NO_2 \rightarrow NO$) at high humidities (5). This problem with the $FeSO_4$ converter can be eliminated if the converter is heated to 32 °C (6).

At this time it is not known what the interfering compound could be since the chemiluminescent instrument used in this study has an optical filter on the photomultiplier tube that cuts off at approximately 6000 Å. Therefore, any excited species emitting at wavelengths longer than 6000 Å would be detected. The sensitivity of the photomultiplier tube, however, drops off at or near 8500 Å. Therefore, the interfering excited intermediate would have to emit between these wavelength limits (6000–8500 Å).

Ozone, when irradiated in the presence of chlorine, reacts very quickly (7), presumably as a result of the fast reaction, $Cl + O_3 \rightarrow ClO + O_2$. By analogy, it is postulated that similar reactions occur in the thermocatalytic degradation of chlorine-containing compounds. Thus, a compound like trichloroacetyl chloride is first catalytically degraded by the hot carbon converter to ClO or ClO_2 and CO_2. The ClO or ClO_2

Table I. Interferences of Halogen-Containing Compounds on NO_x Measurements

	Initial response, ppm		Final response, ppm		% Change in response		
Number	NO	NO_x	NO	NO_x	NO	NO_x	Comments
1	<0.001	0.100	<0.001	0.18	0	+80	5 ppm Phosgene added
2	<0.001	0.100	<0.001	0.43	0	+330	5 ppm Phosgene +8 ppm HCl
3	<0.001	0.140	<0.001	0.145	0	+3.57	0.7 ppm HCl added
4	<0.001	0.140	<0.001	0.170	0	+21.4	0.7 ppm HCl + 0.5 ppm phosgene
5	<0.001	0.140	<0.001	0.185	0	+32.1	0.7 ppm HCl + 1 ppm phosgene
6	0.01	0.17	0.01	0.19	0	+11.76	5 ppm Cl_2 added
7	0.01	0.255	0.01	0.255	0	0	00.5 ppm HCl added
8	0.01	0.255	0.01	0.260	0	+1.96	5 ppm HCl added
9	<0.001	0.125	<0.001	0.142	0	+13.6	1 ppm Trichloroacetyl chloride added
10	<0.001	0.125	<0.001	0.435	0	+248	5 ppm Trichloroacetyl chloride added
11	<0.001	0.320	<0.001	0.32	0	0	0.1 ppm Trichloroacetyl chloride added
12	<0.001	0.320	<0.001	0.55	0	+71.8	2 ppm Trichloroacetyl chloride added
13	<0.001	0.160	1<0.001	0.160	0	0	1.5 ppm Tetrachloroethylene
14	0.0215	0.150	0.02	0.165	−6.97	+10	1 ppm Cl_2 added
15	0.015	0.109	0.014	0.120	−6.66	+10.1	Converter temp raised by 20 °C, 1 ppm Cl_2 added
16	0.001	0.002	0.001	0.026	0	+1200	1.2 ppm Cl_2 added
17	0.001	0.002	0.001	0.04	0	+1900	Same as above, but temp of converter raised by 20 °C
18	0.220	0.226	0.215	0.242	−2.27	+7.07	1 ppm Cl_2 added
19	<0.001	0.001	<0.001	0.005	0	+500	2 ppm Trichloroacetyl chloride
20	<0.001	0.001	<0.001	>0.5	0	+∞	50 ppm Trichloroacetyl chloride

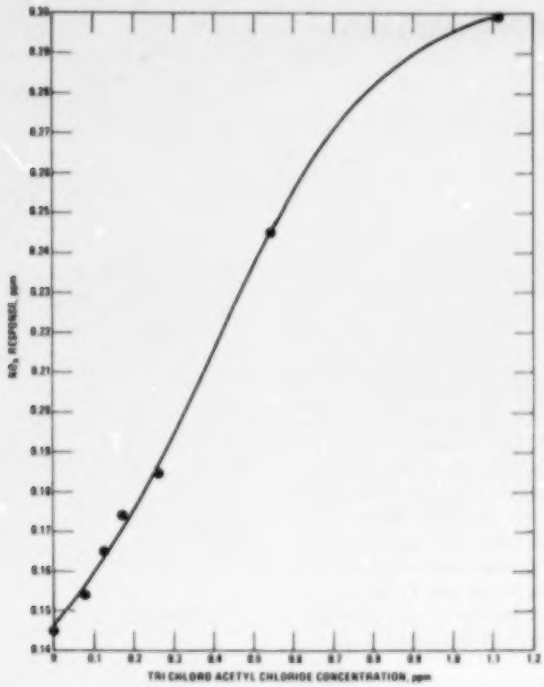

Figure 3. Interference of trichloroacetyl chloride to 0.145 ppm of NO_x

may enter the reaction chamber of the NO_x detector and undergo either $2ClO \rightarrow Cl + ClO_2$ or $ClO_2 \xrightarrow{M} Cl + O_2$. The chlorine atom can then react with ozone to produce an excited oxygen molecule that will emit within the allowed 6000–8500 Å region (7620 Å or the "dimol" 6340 Å emission from singlet oxygen).

Additional work will be needed to substantiate this hypothesis.

Conclusions

Commercial chemiluminescent NO–NO_2 analyzers using heated carbon converters show anomalous behavior when halogen-containing compounds are present. The response appears to be nonquantitative. The implications of these observations are probably not serious in the case of most ambient air analyses, since the concentrations of the halogenated species are in the low ppb levels. However, in smog chamber studies or in areas where the halocarbon levels are high (production areas), the reported measurement of NO_2 may be erroneously high. Under these conditions, a ferrous sulfate converter should be considered.

Literature Cited

(1) Joshi, S. B., masters thesis, University of North Carolina, Chapel Hill, N.C., Oct. 1973.
(2) Winer, A. M., Peters, J. W., Smith, J. P., Pitts, J. N., *Environ. Sci. Technol.*, **8**, 1118 (1974).
(3) Saltzman, B. E., *Anal. Chem.*, **26**, 1949 (1954).
(4) Gay, B. W., Hanst, P. L., Bufalini, J. J., Noonan, R. C., *Environ. Sci. Technol.*, **10**, 58 (1976).
(5) Spicer, C. E., Gemma, J. L., Schumacher, P. M., Ward, G. F., "Fate of Nitrogen Oxides in the Atmosphere", second year rep. to Coordinating Research Council, CAPA-9-71, Aug. 1976.
(6) Stevens, R. K., Environmental Protection Agency, Research Triangle Park, N.C., private communication, 1977.
(7) Gay, B. W., *ibid.*, 1976.

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